

## **Global Carbon Data Management and Synthesis Project**

Christopher L. Sabine<sup>1</sup>, Richard A. Feely<sup>1</sup>, Steve Hankin<sup>1</sup>, Rik Wanninkhof<sup>2</sup>, Tsung-Hung Peng<sup>2</sup>,  
Alex Kozyr<sup>3</sup>, Robert Key<sup>4</sup>, Frank Millero<sup>5</sup>, Andrew Dickson<sup>6</sup>

<sup>1</sup> NOAA Pacific Marine Environmental Laboratory, Seattle, WA

<sup>2</sup> NOAA Atlantic Oceanographic and Meteorological Laboratory, Miami FL

<sup>3</sup> Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, TN

<sup>4</sup> Princeton University, Princeton, NJ

<sup>5</sup> University of Miami, RSMAS, Miami, FL

<sup>6</sup> Univ. of California San Diego, Scripps Institution of Oceanography, La Jolla, CA

## **PROJECT SUMMARY**

The ocean plays a critical role in the global carbon cycle as it is a vast reservoir of carbon, naturally exchanges carbon with the atmosphere, and consequently takes up a substantial portion of anthropogenically-released carbon from the atmosphere. Although the anthropogenic CO<sub>2</sub> budget for the last two decades, i.e. the 1980s and 1990s, has been investigated in detail (Prentice et al., 2001), the estimates of the oceanic sink were not based on direct measurements of changes in the oceanic inorganic carbon.

Recognizing the need to constrain the oceanic uptake, transport, and storage of anthropogenic CO<sub>2</sub> for the anthropocene and to provide a baseline for future estimates of oceanic CO<sub>2</sub> uptake, two international ocean research programs, the World Ocean Circulation Experiment (WOCE) and the Joint Global Ocean Flux Study (JGOFS), jointly conducted a comprehensive survey of inorganic carbon distributions in the global ocean in the 1990s (Wallace, 2001). After completion of the US field program in 1998, a five year effort – the Global Ocean Data Analysis Project (GLODAP) - was begun to compile and rigorously quality control the US and international data sets including a few pre-WOCE data sets in regions that were data limited (Key et al., 2004). Although these data have improved our understanding of the spatial distributions of natural and anthropogenic carbon in the ocean, they have yet to be fully exploited to examine the mechanistic controls on these carbon distributions or to understand the temporal patterns of variability.

Most of the approaches used to estimate anthropogenic CO<sub>2</sub> in the oceans are based on assumptions of steady state circulation and constant biology. It is becoming increasingly apparent that these assumptions may not hold in a global change environment. The most important component of an assessment of ocean biogeochemical change, whether of natural or anthropogenic origin, is high-quality observations. The WOCE/JGOFS data set provides an important point of reference for ocean carbon studies. Many other useful data sets have not been analyzed in such a context, however because there has not been a coordinated effort to bring these data together and no data management system to make navigation and exploitation of these data convenient.

The NOAA Office of Climate Observation's Carbon Network (hydrographic sections, underway pCO<sub>2</sub>, and CO<sub>2</sub> moorings) is a valuable contribution to the Global Ocean Observing System (GOOS) and Global Climate Observing System (GCOS). It is not sufficient, however, simply to collect and archive the data, if we expect the data to improve our understanding of the global carbon cycle and the role of the ocean in climate change.

Recognizing the need for proper data management and synthesis, NOAA's Office of Climate Observations (OCO) has funded several projects to manage and perform an initial interpretation of the data collected from the Carbon Network. Because three of these OCO projects are very closely linked

and often work together to generate an end product, we have combined the projects into one management and synthesis project as of this report. The goal of the Global Carbon Data Management and Synthesis Project is to work together with the OCO carbon measurement projects to take the fundamental carbon observations and turn them into products that are useful for scientists and the public for understanding the ocean carbon cycle and how it is changing over time. This effort ranges from ensuring that the observations are of the highest quality and are mutually consistent with each other to combining the observations into a common data set that is available and easy for the community to use and explore to evaluating the time rate of change in global ocean carbon uptake and storage. This project brings together ocean carbon measurement experts, information technology experts and data managers to ensure the most efficient and productive processing possible for the OCO carbon observations.

## **BACKGROUND**

Although ocean carbon uptake and storage plays a critical role in influencing global climate change, the community involved in studying ocean carbon is not as large nor is it as geared towards operational activities as the climate and physical oceanographic communities. There are no operational data centers ready to take the basic carbon observations and turn them into products like the climate forecasts or reanalysis products. As a consequence, the ocean carbon community is expected to provide the public with advanced analysis products, like global CO<sub>2</sub> flux maps or maps of the patterns of CO<sub>2</sub> uptake and storage, in addition to the basic observations. The generation of these products is the objective of this project, but it is a somewhat complicated process because it involves several data manipulation steps and coordination with many other investigators. For this report we divide the process into three categories: measurement coordination and initial quality control, data management and contextual quality control, then synthesis and interpretation.

The number of observations needed to address a global issue like ocean carbon uptake and storage is well beyond the capabilities of one lab or even one country. Thus, there are many laboratories from several countries involved in the assessment of global carbon distributions. To produce the greatest return on the US investment in ocean carbon measurements, we must ensure that all of the US laboratories are using consistent cutting-edge techniques, are assessing and documenting the data quality, and are coordinating the US measurements with the international programs so that once the data are combined we get the most extensive coverage possible. This is the measurement coordination and initial quality control portion of this project. Once the data are collected and the initial data quality has been documented, then the data must be pulled into a data management system that brings the individual laboratory data sets together into a common data base. At this point the data sets are large enough that it is awkward to manipulate without a data visualization program. Once the data set is assembled, the internal consistency of the data relative to any crossing or historical data must be checked. This is the data management and contextual quality control portion of the project. The final step in the process is taking the data set and examining it to understand how the current carbon distributions have changed and the mechanisms responsible for the observed changes. This last step is an evolving set of analyses that is continually improved and adapted as additional data are added to the data set. Each of these three steps is related and often requires iterative refinements of the previous steps to develop the final products leading to improved estimates of ocean uptake and storage.

The OCO ocean carbon network makes two basic types of observations: surface CO<sub>2</sub> observations with ships of opportunity and moorings and water column carbon observations with repeat hydrography cruises. The Global Carbon Data Management and Synthesis Project addresses both

observation types. Because surface observations are collected in a different manner and have different requirements for developing the final product than the repeat hydrography data, the data management for these two data types is discussed separately. The activities and accomplishments for both data types in FY07 are discussed below.

## **ACCOMPLISHMENTS**

The funds received for Global Carbon Data Management and Synthesis Project were instrumental in providing data to the scientific community at large; for promoting and allowing the global synthesis and interpretation of national and international surface and water column carbon data; and integration of the carbon program elements within the NOAA Climate Observation Program.

### **Measurement Coordination and Initial Quality Control**

The first NOAA carbon principal investigator meeting was hosted by AOML in Miami in February 2007. This meeting was attended by most investigators involved in the four Climate Observation Program carbon projects: repeat hydrography, CO<sub>2</sub> measurements from ships, CO<sub>2</sub> measurements from buoys, and synthesis and data management. The meeting also included program managers from the Climate Observation Program and Global Carbon Cycle Program and worked to improve coordination of the NOAA carbon projects and develop consensus on "best practices" for measurements and data management. In addition, members of the Global Carbon Data Management and Synthesis Project participated in a variety of national and international workshops to improve coordination between the NOAA carbon program and the national and international carbon community:

- Sustained Indian Ocean Biogeochemistry and Ecological Research (SIBER) Workshop, Goa, India, October 1-8, 2006
- CLIVAR Global Synthesis and Observations Panel SSG meeting, La Jolla, CA, Dec. 8-9
- North American Carbon Project PI meeting, Colorado Springs, CO, January 22-24, 2007
- Joint Canada-US-Mexico NACP meeting, Colorado Springs, CO, January 25-26, 2007
- Atlantic Ocean Carbon Synthesis Meeting, Kiel Germany, March 21-23, 2007
- Ocean Surface pCO<sub>2</sub> and Vulnerabilities Workshop, Paris, France, April 11-13, 2007
- Anthropogenic Stresses on Ocean Ecosystems Workshop, Seattle, WA, April 23-24, 2007
- Ocean Carbon and Biogeochemistry annual workshop, Woods Hole, MA, July 23-26, 2007
- NOAA GCC program PI meeting, Silver Spring MD, September 10-11, 2007

### ***Repeat Hydrography***

DIC data from all new repeat hydrography cruises up through 2007 as well as the hydrographic, nutrient and CFC data from all NOAA led cruises have gone through post cruise calibration and corrections. The responsible PIs have completed the first level of quality control and submitted finalized data to the Carbon Dioxide Information Analysis Center (CDIAC) and the Clivar Carbon and Hydrographic Data Office (CCHDO). The data and the flags are double checked by both CDIAC (Kozyr) and Princeton (Key). Any discrepancies are resolved, though that is seldom necessary. Both the early data submission and the extremely high quality of the CLIVAR carbon measurements have greatly simplified this procedure. At CDIAC, Kozyr has refined the CLIVAR web presentation so that it is simple for a user to access CLIVAR data as well as data from previous cruises along the same sampling

line. This web organization makes it easy for any end user to see which sections have been repeat-sampled and to download the appropriate data for subsequent investigation.

CDIAC has processed all new Repeat Hydrography sections: P16S\_2005, P16N\_2006, I8S\_2007, I9N\_2007. CDIAC also works closely with the CCHDO to merge the final carbon data with the final hydrographic data and ensure that the latest results are available to the community in a variety of formats. All of the latest repeat hydrography data have also been added to the CDIAC Mercury and WAVES (<http://cdiac3.ornl.gov/waves/>) data management tools. CDIAC numeric data packages (NDPs) for the A20, P02 and P16S cruises have not been published yet because the alkalinity data on these cruises have not been finalized.

All future cruise plans are coordinated with the international community through the International Ocean Carbon Coordination Project (IOCCP) and the international CLIVAR office.

### ***Surface CO<sub>2</sub>***

CDIAC received and processed new data from the following VOS lines: Nuka Arctica 2005 lines (Norway), Skaugran 1995 -1999, Alligator Hope 1999-2001, Pyxis 2001-2006, Ryofu Maru 1989-2007, Keifu Maru 2001-2007, and Kofu Maru 1998-2002 (all Japan), Aurora Australis 1993 – 2002 cruises (Australia), Explorer of the Seas 2004-2006 (USA). Data from the OCO moored CO<sub>2</sub> observations have also been received and processed. All data were quality controlled, evaluated and made available to public through CDIAC VOS web page: [http://cdiac.esd.ornl.gov/oceans/global\\_pco2.html](http://cdiac.esd.ornl.gov/oceans/global_pco2.html). The metadata for these data were added to Mercury: <http://mercury.ornl.gov/ocean/>.

Based on meetings with the international ocean carbon community and from our PI meeting, AOML and PMEL have reprocessed all of our current and historical underway pCO<sub>2</sub> data into a common internationally agreed upon format. Meta-data was updated in the format advocated by the International Ocean Carbon Coordination Panel (IOCCP) and data have been forwarded to the national repository at CDIAC. The moored CO<sub>2</sub> data and meta-data have also been put into the same formats to encourage a better integration of these data streams. The latest surface CO<sub>2</sub> data were also sent to Dr. Takahashi for inclusion in his updated climatology. This marks the first time that the Takahashi climatology will include both underway and moored data. The full Takahashi dataset has been published by CDIAC as a numeric data package NDP-088 (CDIAC-152): *Global Ocean Surface Water Partial Pressure of CO<sub>2</sub> Database: Measurements Performed During 1968–2006 (Version 1.0)*.

During the last fiscal year, new software was written at PMEL to quickly process data files that are transmitted daily via Iridium satellite from the NOAA ships *Ka'imimoana* and *Albert Rickmers*. This software processes the daily data and creates diagnostic plots of pCO<sub>2</sub>, temperature, salinity, barometric pressure, water flow and gas flow. The plots are posted on a newly created internal website and are used as a diagnostic tool for data processing and quality control of the underway pCO<sub>2</sub> data. All current and previous VOS data files are quality controlled using the data submission protocol for ships under the NOAA Office of Climate Observations (OCO) workplan "pCO<sub>2</sub> measurements from ships". After installation of real-time data transmission on the AOML VOS ships, a new download and near-real time display program was produced at AOML to accommodate different origins of the data streams. Data and error reports are transmitted from the ships via Iridium or FTP every morning and checked for instrumental issues.

### **Data Management and Contextual Quality Control**

#### ***Repeat Hydrography***

In collaboration with European partners in the Carboocean effort we are engaged in a major synthesis of data sets in the Atlantic, Arctic and Southern oceans. The focus is on older data (pre-2003) in the Atlantic Ocean and is being collated by Dr. Key of Princeton. Last year Key reported a total collection of 85 cruises and the expectation that “several more” would be obtained by the Carboocean data submission deadline of 12/31/06. Carboocean is a European Union program and European scientists have been the source for virtually all these previously unavailable data. In reality the number of submitted cruises exploded to a total of 169. This incredible increase was largely influenced by the deadline, but also by the fact that the study region was expanded during a meeting late last year in Iceland, to include the entire Arctic Ocean and the Southern Ocean rather than just the North Atlantic and Nordic Seas. The workload implied by this growth combined with the very tight Carboocean time schedule very significantly exceeded what was possible with the support from this grant. Consequently, additional funding was requested from NOAA-OGP via a separate grant. Upon hearing that this proposal would be funded, part time technical help (Xiaohua Lin) was hired at Princeton specifically for data formatting and similar database chores. This new data collection will be known as CARINA after the defunct European project of the same name. Figure 1 shows the CARINA station locations for the cruise data distributed to the working teams in October.

The data from the CLIVAR CO<sub>2</sub> repeat hydrography cruises will be used as a standard against which the CARINA cruises will be compared. As part of this effort, Wanninkhof and Key attended a synthesis meeting at Kiel, Germany in March 2007. At the Kiel meeting it became obvious that the manual secondary QC techniques used during GLODAP would be impossible for this volume of data and time frame. The plan to semi-automate the process was assigned to a software team that included input from Wanninkhof and Key. This software is still evolving and will continue to develop, but sufficiently sophisticated versions are now available on-line and being used by each group. Thus far, the software will automatically identify those stations in a merged dataset which are within given distance of each other and then carry out a routine deep water “crossover” analysis similar to those used in GLODAP. The maximum station separation distance and the list of tested parameters are chosen by the operator. Next, the crossover results are passed to an objective minimizing routine similar to that used by (Johnson et al., 2001). Some CARINA cruises data are now available through the open CDIAC CARINA web site ([http://cdiac.ornl.gov/oceans/CARINA/Carina\\_inv.html](http://cdiac.ornl.gov/oceans/CARINA/Carina_inv.html)). A password protected CARINA web site has been established at CDIAC for secondary QC and synthesis work. AOML leads the effort of secondary quality control of the post-1997 WOCE cruises and CLIVAR/CO<sub>2</sub> cruises in the Atlantic. PMEL is leading the secondary quality control for the Pacific sector of the Southern Ocean. The Carboocean synthesis subgroups are in the process of examining over 800 crossovers for DIC, O<sub>2</sub>, NO<sub>3</sub>, T, S, SiO<sub>2</sub>, and PO<sub>4</sub>.

A similar effort is beginning in the Pacific as part of the North Pacific Marine Science Organization (PICES) section on Carbon and Climate. PMEL investigators (Feely and Sabine) have been PICES members for years. Approximately a year ago PICES PIs decided to construct a data set of historic cruises from their countries similar to CARINA. At the annual meeting, which was held in Victoria, B.C. during October, Japanese scientists presented a list of approximately 200 cruises on which carbon measurements had been made during recent times. The data from about 60 of these cruises had actually been obtained and converted to similar format. Korean attendees (primarily K. Lee) volunteered additional Korean cruises for the collection and communication channels were opened between scientists who are actively trying to recover decades of data from C.-S. Wong’s Canadian laboratory.

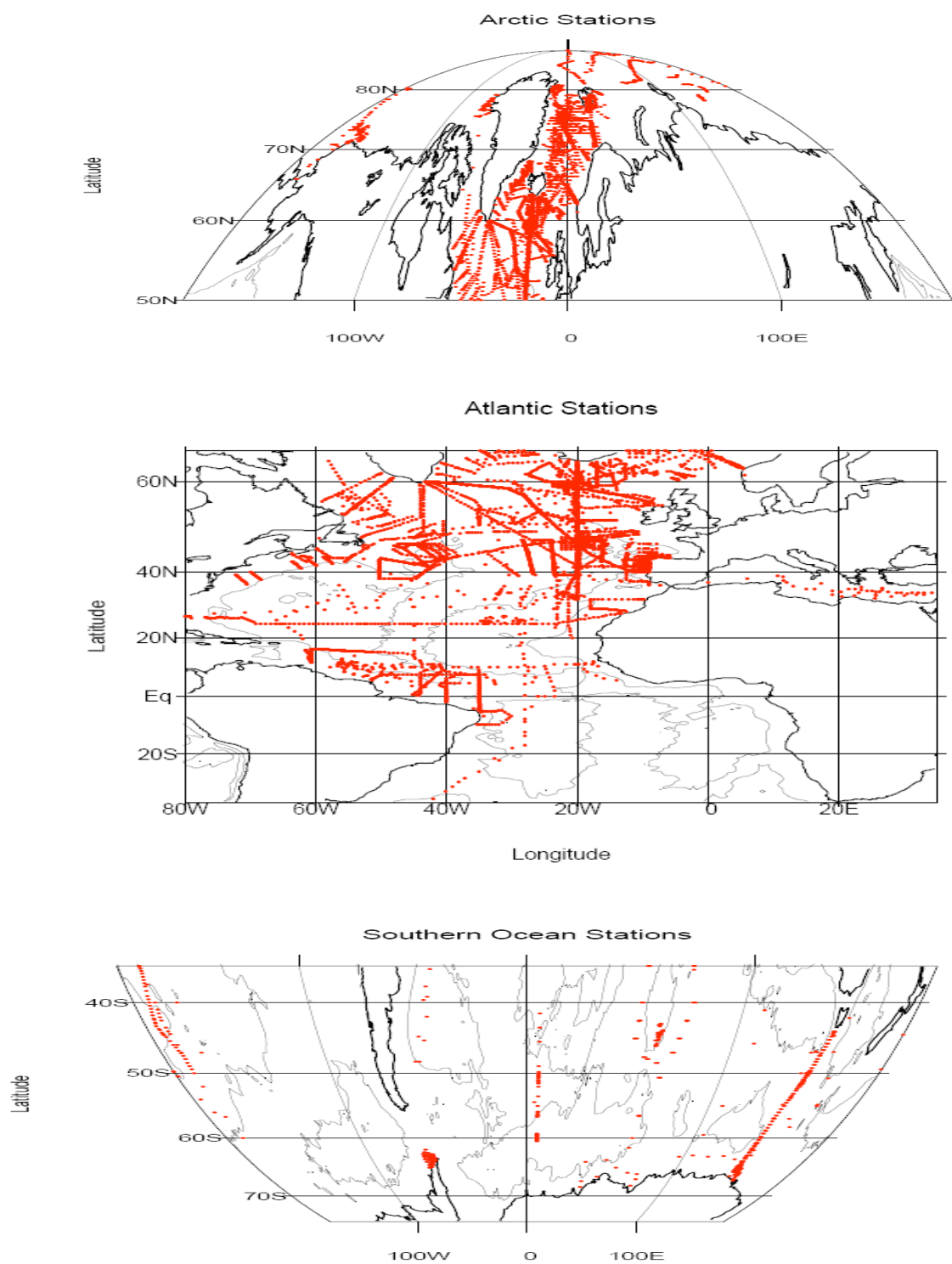


Figure 1. Maps of new stations (beyond GLODAP) compiled for CARINA dataset and international data synthesis efforts.

At the meeting various rules for data sharing, etc. were discussed and agreed. In most respects the operating procedures will be quite similar to those used for Carbocean/CLIVAR. With collaborations from Toru Suzuki, MIRC (Japan), CDIAC has started to compile the PICES database for the secondary quality control effort ([http://cdiac.ornl.gov/oceans/PICES/PICES\\_table.html](http://cdiac.ornl.gov/oceans/PICES/PICES_table.html)). Initial quality control and additional formatting will be done at Princeton and work groups will eventually be formed to carry out secondary QC and subsequent science.

One major difference between the PICES and CARINA efforts is that the PICES work will not be funded by a central organization. That is, PICES does not fund science it only covers travel expenses for PICES members to the annual meeting. This funding arrangement is identical to that of the original CARINA collaboration of the 1990s and in that case the project was a failure. We are hopeful that this result can be reversed. That optimism is based on three key factors: (1) a few Japanese scientists with secure funding have a strong vested interest in the project (2) the existence and full cooperation of CDIAC from the outset and (3) the experience provided by the U.S. participants. In the worst case scenario, secondary QC tasks could be carried out primarily by the funded Japanese and U.S. participants. This would be far from ideal and would significantly extend the required analytical time, but should eventually produce a valuable data product for the North Pacific.

### ***Surface CO<sub>2</sub>***

Working through the IOCCP and EU Carbocean project, Global Carbon Data Management and Synthesis Project members helped promote and establish a standard global surface CO<sub>2</sub> data set for the international community. This effort builds on the work started in 2001 as part of the EU ORFOIS project by Dorothee Bakker (UEA) and now continues as part of the Carbocean project. Benjamin Pfeil and Are Olsen (Bjerknes Centre for Climate Research) have compiled more than 1250 cruises from 1972 - 2007, with approximately 4.5 million measurements, into a dataset with a common format that has undergone standard 1<sup>st</sup> level Quality Control procedures. These data will be submitted to CDIAC by the end of calendar year 2007. Project members will continue to work with the international community to develop regional teams to conduct the second level quality control in a manner similar to the CARINA data discussed in the previous section.

In FY07 PMEL continued development of the Ocean Carbon Data Management System (OCDMS) with a focus on underway data as the primary area for data management work. The LDEO (Takahashi) consolidated collection was the target of much of these efforts guided by the strategy that, through addressing this dataset -- the largest assembled collection of underway cruises -- the techniques and tools needed to handle individual OCO-sponsored carbon measurement cruises would advance as well. Indeed, we also applied these tools to individual cruise data from PMEL and AOML. The work involved developing a new database schema; tools and procedures for ingesting the data; quality control filters; tools and techniques for high speed retrieval of selected subsets from the collection; and an LAS-based system (user interface and products) for visualization of the data and interaction with it. A version of the work was presented by Jon Callahan to the Carbon Science Team meeting in Miami in February, 2007. A more recent update was presented by Steve Hankin at the NOAA Global Carbon Cycle PI meeting in September.



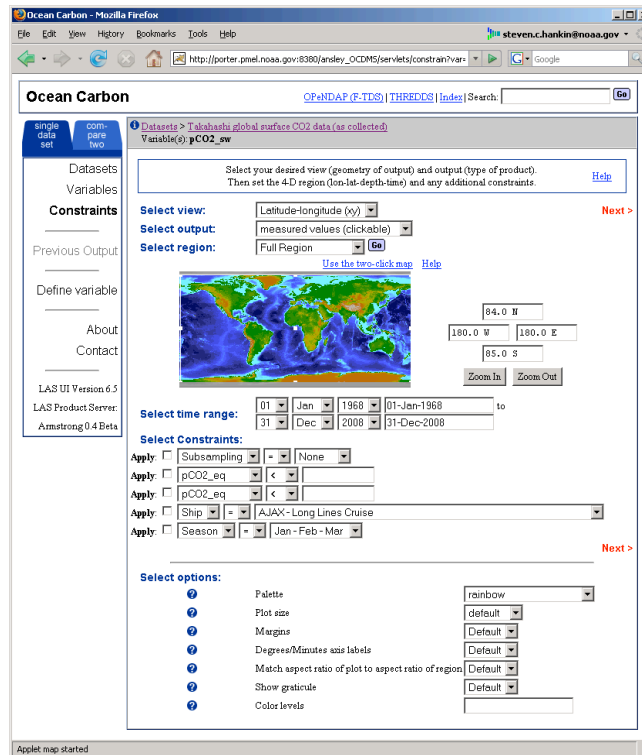


Figure 2. OCDMS User Interface snapshot

The process of ingesting data as a collection into a database provides a final filter on several aspects of quality control. The filters that were developed for the OCDMS and utilized on the LDEO collection ingested over 3.2 million records from which they flagged 34,485 (1.1%) as invalid due to out-of-range (not plausible) values and 14379 (0.4%) as duplicates. (Duplicate records can cause mis-weighting during analyses.) These errors were reported back to LDEO, and have been incorporated into the recently released update of the LDEO database.

To achieve adequate interactive performance it was necessary to derive hourly, 4x daily and daily subsets of the data in the database as well as the full resolution tracks. Typically the system determines which subsampled level of data to access based upon the scope of the request, though the user can override this. In the screen snapshot of the user interface (Figure 2) this control is visible as the Subsampling constraint. An example illustrating the importance of the subsampled database tables is found in Figure 3 (left), where we see a global snapshot of pCO<sub>2</sub> seawater for 1968 through the present. The LAS system delivers such a figure in a matter of seconds, although the full resolution data contain millions of observations.

Exploratory styles of interacting with the data are also provided. For example, zooming into a localized view of data (Figure 3 right) and viewing the relationships between properties. The ability to constrain data queries based upon essential metadata is an important requirement of the system. In Figure 2 above we see controls to constrain searches based upon ship ID and seasonality. Seasonality is of particular importance in interpreting the data. Further constraint options may be added in the future as requested by carbon scientists.



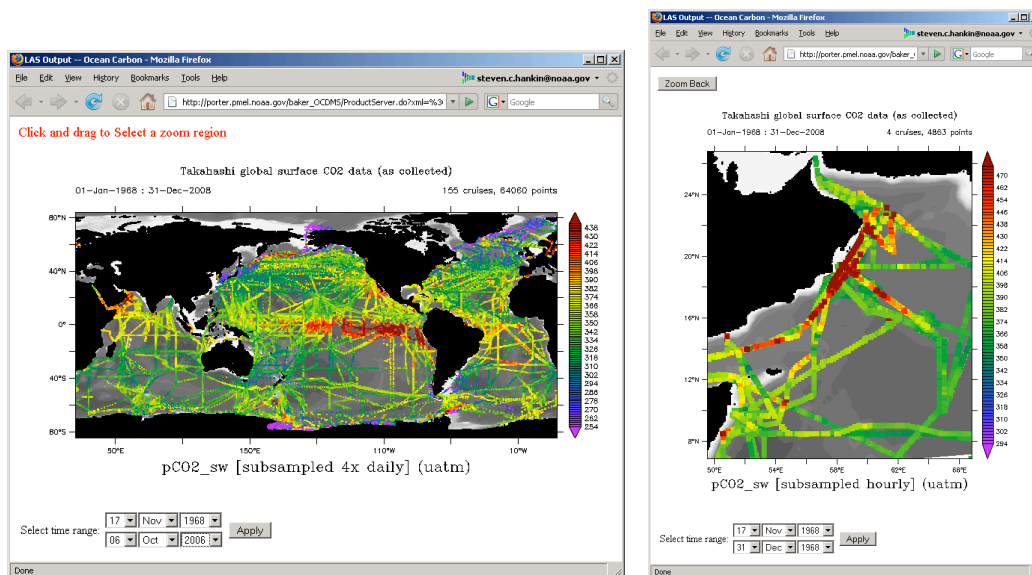


Figure 3. pCO<sub>2</sub> seawater from LDEO 1968 to present globally (left) and zoomed (right)

Figure 4 illustrates the display of ocean carbon maps onto the Google Earth<sup>®</sup> application. While not a specifically pressing need of the carbon science community, tools such as Google Earth<sup>®</sup> provide outreach to other communities and demonstrate the interoperability of the OCDMS with other applications.

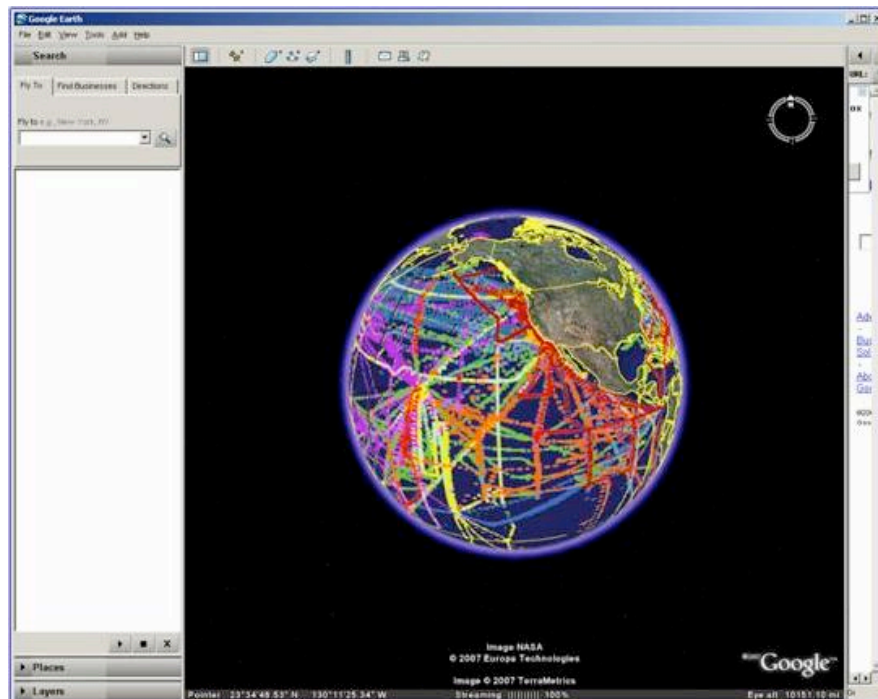


Figure 4. Carbon map displayed on Google Earth<sup>®</sup>

## Synthesis and Interpretation

### *Repeat Hydrography*

Global Carbon Data Management and Synthesis Project members have continued to investigate ocean carbon system variability using both the existing GLODAP dataset as well as new Repeat Hydrography cruises. This work has focused primarily on understanding the natural variability in the ocean carbon system and how these changes can be distinguished from the expected secular trends from rising atmospheric CO<sub>2</sub>.

Three publications on the changes in the Atlantic have been written with PI's of this program as co-author (Chanson et al., 2007; Levine et al., 2007; Wanninkhof et al., 2007). The work shows that the anthropogenic CO<sub>2</sub> increase is unequivocal but that quantification is very dependent on approach with estimates for the Atlantic ranging from 0.4 to 0.8 mol/m<sup>2</sup>/yr with most converging at 0.6 mol/m<sup>2</sup>/yr. On a basin-scale several approaches yield similar estimates but regional differences and biases are very apparent. Comparisons of the basin-wide patterns of decadal anthropogenic CO<sub>2</sub> uptake based on several different permutations of the multi-linear regression approach are provided in Figure 5. Modeling efforts using the NCAR community model confirm the magnitude and general location of decadal variability in the sub-polar gyres that can be primarily attributed to changes in ventilation (Levine et al., 2007).

Ever since GLODAP produced the first global estimates of the oceanic anthropogenic CO<sub>2</sub> distribution, one very curious result has remained: the fact that the near surface anthropogenic CO<sub>2</sub> concentrations were so much higher in the Atlantic than in the Indo-Pacific. When first noted, C. Sabine and K. Lee rechecked the GLODAP Atlantic methods and results. Their efforts indicated that methodology variations might explain some of the difference, but the major portion appeared to be real. Since then R. Toggweiler (GFDL) along with J. Sarmiento and R. Key (Princeton) have been trying to understand the discrepancy. Over the years several theories have been proposed, however, in each case testing eventually killed all previous ideas. Very recently Toggweiler proposed a new theory. As with some of the previous ideas, this one hinges on the fact that most of the global river input is into the Atlantic and that riverine chemistry (concentrations) is significantly different than the ocean for both DIC and alkalinity. This chapter of the investigation is just starting, however, it differs from previous ones both in simplicity and the fact that longer time scale processes are included. If successful, a report of this research will be included in the 2008 annual report.

The Pacific has been examined by the group using a couple of different approaches. For example, isopycnal analyses have been used to investigate the temporal changes in DIC between the 1991 and 2006 occupations of P16N. Comparisons of DIC along isopycnal surfaces with sigma-theta of 26.0, 26.2, 26.4, 26.6, 26.8, 27.0, and 27.2 for P16N. The DIC increases vary on each isopycnal, with 2.4 μmol/kg along 27.2, and 18.0 μmol/kg along 26.4. Using the estimated thickness of isopycnal horizons between 15°N and 45°N, we obtained a mean DIC inventory change of 0.58 μmol/kg/yr in the North Pacific between 1991 and 2006. For the South Pacific, the DIC increase is apparently much faster. We have seen significant DIC increases along each isopycnal horizons, on the order of 20 μmol/kg from 26.0 to 27.2. Based on the estimated thickness of isopycnal layers between 15°S and 40°S, the mean DIC inventory change is estimated to be 1.61 μmol/kg/yr for the period from 1991 to 2005.

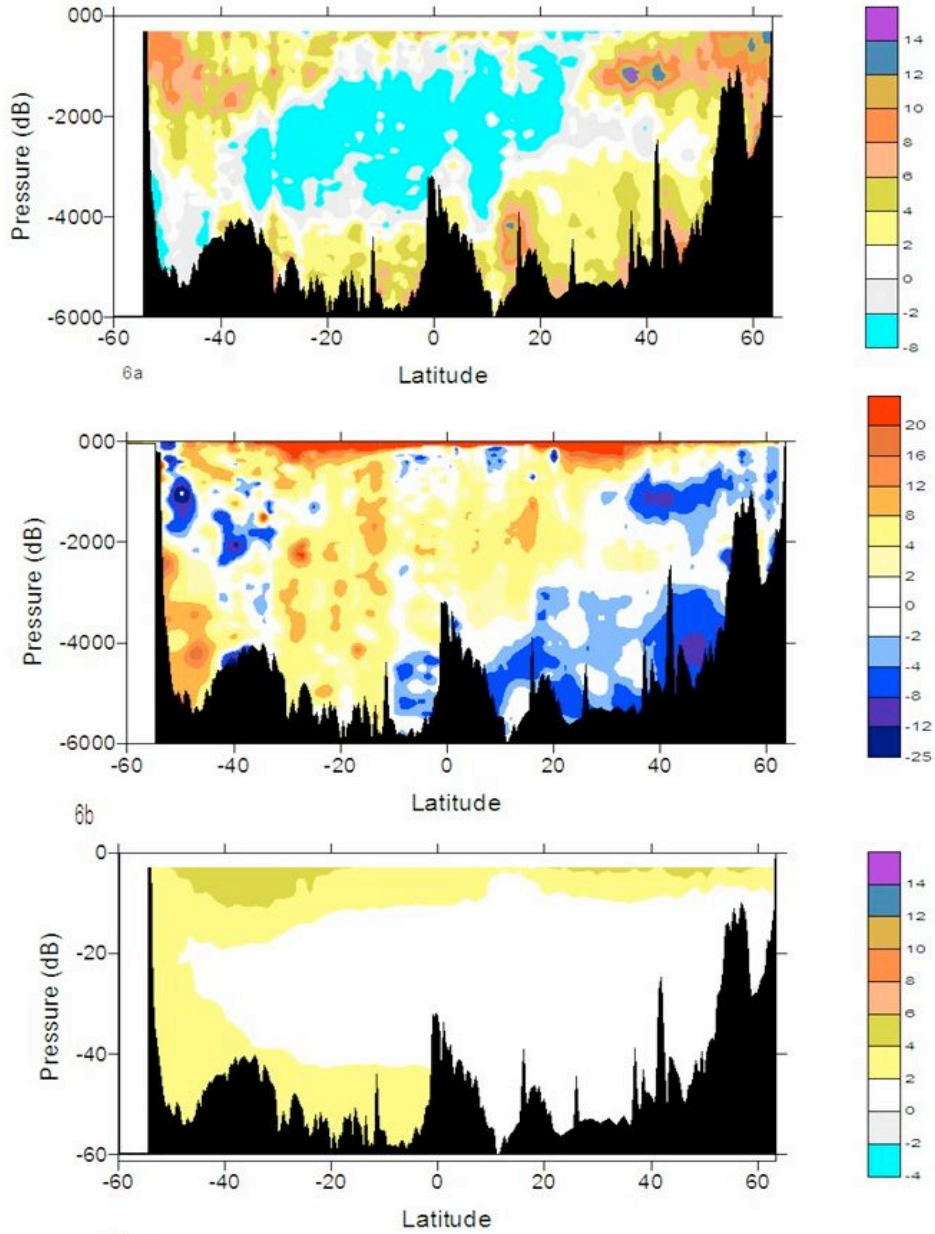


Figure 5: Different multi linear regression (MLR) approaches to estimate the anthropogenic CO<sub>2</sub> increase over the last decade for the full water column along line A16 through the middle of the Atlantic Ocean utilizing S,T, AOU, NO<sub>3</sub>, and SiO<sub>4</sub> as input parameters. (a) MLR determined from 1989/1993 data subtracted from 2003/2005 DIC data. (b) 1989/1993 DIC data subtracted from a MLR created with the 2003/2005 DIC data. (c) MLR determined from 1989/1993 data subtracted from the MLR determined with the 2003/2005 data using S, T, AOU, NO<sub>3</sub>, and SiO<sub>4</sub> from 2003/2005. The approach is referred to as the extended multi-linear regression (e-MLR). Note the differences in scale.

We have also used the extended multiple linear regression (eMLR) technique to investigate changes over the last decade in DIC inventories on a meridional line (P16 along 152°W) up the central Pacific and on a zonal line (P02 along 30°N) across the North Pacific (Sabine et al., 2007). Maximum changes in the total DIC concentrations along P02 are 15-20  $\mu\text{mol kg}^{-1}$  over 10 years, somewhat higher than the  $\sim 1 \mu\text{mol/kg/yr}$  increase in DIC expected based on the rate of atmospheric CO<sub>2</sub> increase. The

maximum changes of 15-20  $\mu\text{mol/kg}$  along the P16 line over the 14/15 year time frame fit with the expected magnitude of the anthropogenic signal, but there is a deeper than expected penetration of the signal in the North Pacific compared to the South Pacific. The effect of varying circulation on the total DIC change based on decadal alterations of the apparent oxygen utilization rate is estimated to be greater than 10  $\mu\text{mol/kg}$  in the North Pacific, accounting for as much as 80% of the total DIC change in that region (Figure 6). The average anthropogenic  $\text{CO}_2$  inventory increase along 30°N between 1994 and 2004 was 0.43  $\text{mol/m}^2/\text{yr}$ , with much higher inventories in the western Pacific. Along P16, the average Northern Hemisphere increase was 0.25  $\text{mol/m}^2/\text{yr}$  between 1991/1992 and 2006 compared to an average Southern Hemisphere anthropogenic  $\text{CO}_2$  inventory increase between 1991 and 2005 of 0.41  $\text{mol/m}^2/\text{yr}$ .

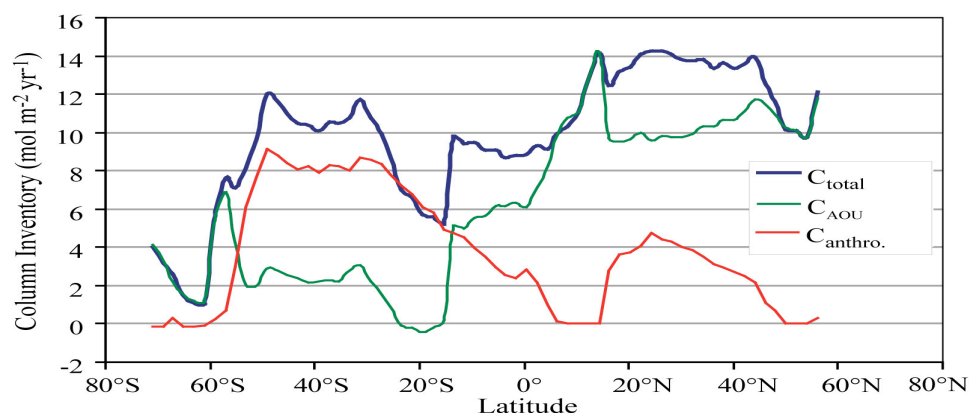


Figure 6. Plot of column inventories along P16N (150°W) showing the total inventory, the inventory attributed to circulation changes as estimated from AOU and the anthropogenic  $\text{CO}_2$  inventory.

The Repeat Hydrography program began surveying the Indian Ocean with the I8S/I9N line, nominally along 95°E, in February to March 2007. The DIC data have been finalized and submitted to CDIAC, but we are just starting to look at the data in terms of secondary quality control and decadal changes. Comparison of deep data with the previous WOCE cruises shows that both cruises have very high quality data. Figure 7 shows the initial comparison of measured values along the section. This figure clearly indicates large changes in DIC over the time period, but additional analyses must be made to evaluate whether these changes directly result from anthropogenic  $\text{CO}_2$  uptake or not.

The Princeton group has been examining model and data derived results comparing data from reoccupations separated by 6 months up to 2 years. With these short time intervals, differences in DIC along a section should be totally dominated by processes other than invasion of anthropogenic  $\text{CO}_2$  from the atmosphere. This research is still in progress, but the model results confirm the findings from the Pacific that physical changes alone can generate DIC changes along a section that are as large as the expected decadal anthropogenic  $\text{CO}_2$  invasion signal. On shorter time scales, the physical changes along a section can be very significant in the upper water column. The model suggests that some but not all of the resulting DIC change is reflected in oxygen change. Over the next few months we will be using model output to help understand what is causing these differences. We are hopeful that this work will eventually lead to improved methods for quantifying both natural variability and anthropogenic  $\text{CO}_2$  uptake.

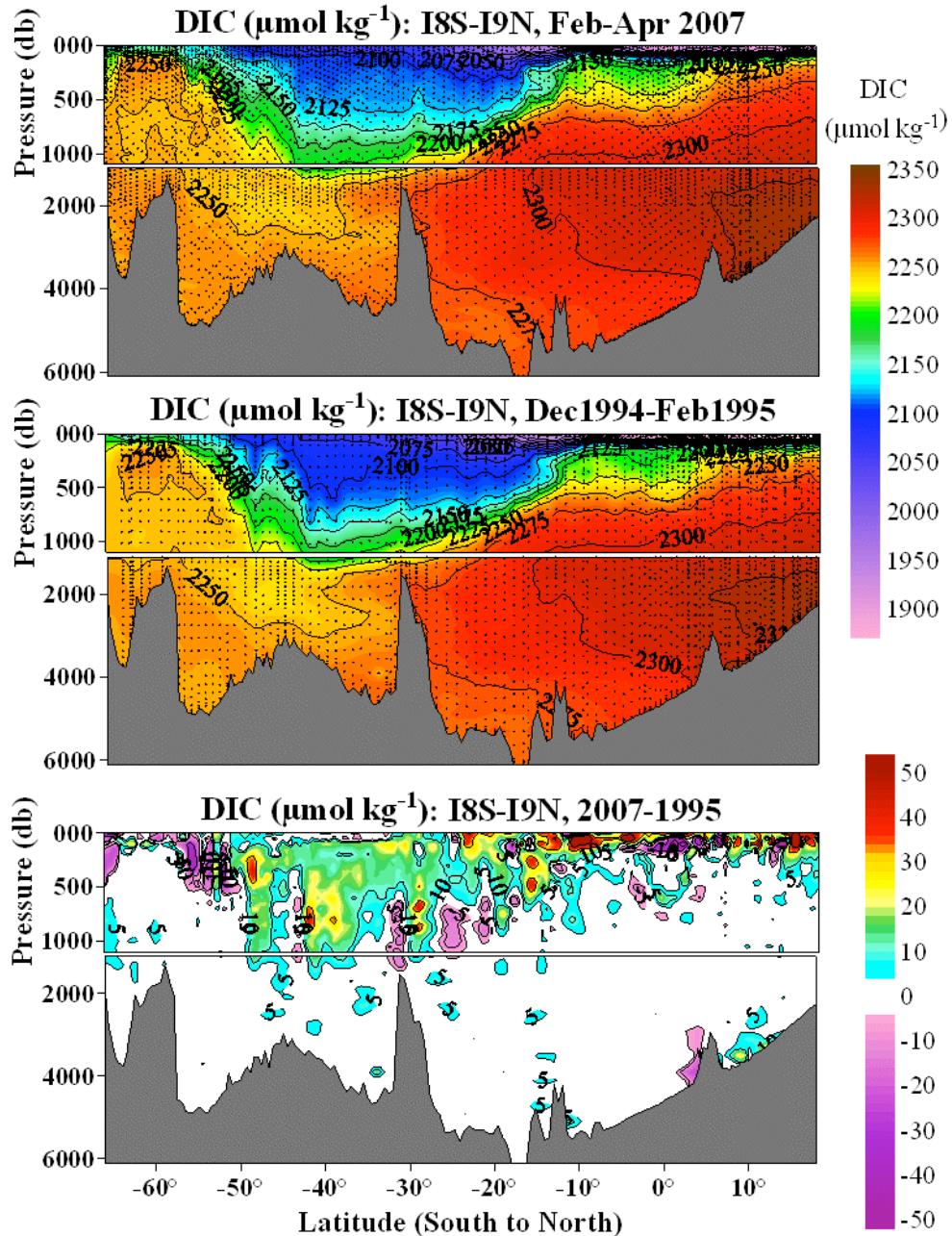


Figure 7. Meridional sections of DIC in the eastern Indian Ocean from the 1995 WOCE survey, from the 2007 repeat hydrography cruise, and a plot of the difference between the measured values.

### ***Surface CO<sub>2</sub>***

Global Carbon Data Management and Synthesis Project members are also investigating ocean carbon system variability in the surface ocean using both the existing GLODAP data set as well as new data. This work has focused primarily on understanding the time and space scales of variability of CO<sub>2</sub> in the global ocean.

In McNeil et al. (2007), we produced an empirical estimate of the CO<sub>2</sub> flux in the Southern Ocean based on near surface DIC and alkalinity data from GLODAPv1.1 (Key et al., 2004) plus additional data provided by N. Metzl. The empirical relationships were multiple linear regressions in



form, but limited to hydrographic parameters and nutrients for fitting. The equations were able to reproduce surface DIC and alkalinity (normalized to constant salinity) values to within 8  $\mu\text{mol/kg}$ . The equations were used with global climatologies of the fitting parameters to investigate seasonal variations in the surface concentrations of DIC and alkalinity. The procedure was also used to approximate surface  $\text{pCO}_2$  concentrations and to subsequently calculate air-sea  $\text{CO}_2$  fluxes. In general the flux estimates were similar to those reported by (Takahashi et al., 2002), and somewhat higher than inversion based estimates.

In Sweeney et al. (2007) we used the GLODAPv1.1 radiocarbon data, augmented in the far North Atlantic using an approximation technique, to re-estimate the global mean air-sea gas exchange rate based on the bomb-produced radiocarbon inventory. The method was a natural extension of that originally used by (Broecker and Peng, 1982) and (Broecker et al., 1985). The derived gas exchange rates were lower than Broecker's estimates and Wanninkhof (1992) estimate. The total inventory of bomb-produced radiocarbon in the ocean (from this work) is now in agreement with global budgets based on radiocarbon measurements made in the stratosphere and troposphere.

In Takahashi et al. (2007) a climatological mean distribution for the surface water  $\text{pCO}_2$  over the global oceans in non-El Nino conditions was constructed with spatial resolution of  $4^\circ$  (latitude)  $\times$   $5^\circ$  (longitude) for a reference year 2000 based upon about 3 million measurements of surface water  $\text{pCO}_2$  obtained from 1970 to 2006. Seasonal changes in the surface water  $\text{pCO}_2$  and the sea-air  $\text{pCO}_2$  difference over four climatic zones in the Atlantic, Pacific, Indian and Southern Oceans are presented. The annual mean for the net sea-air  $\text{CO}_2$  flux over the global oceans is estimated to be  $1.4 \pm 0.7 \text{ Pg-C/yr}$ . Taking the pre-industrial steady state ocean source of  $0.4 \pm 0.2 \text{ Pg-C/yr}$  into account, the total ocean uptake flux including the anthropogenic  $\text{CO}_2$  is estimated to be  $1.8 \pm 0.7 \text{ Pg-C/yr}$  in 2000.

Using the approach described in (Lee et al., 1998), and (Park et al., 2006) we have estimated the interannual variability in air-sea  $\text{CO}_2$  fluxes from 1989-2006 using the new climatology of Takahashi et al. (2007). The effect of this new climatology on the past estimate of variability from 1990-2006 is shown in figure 8. The newer results show a 30 % increase in interannual variability as determined by the difference in standard deviation.

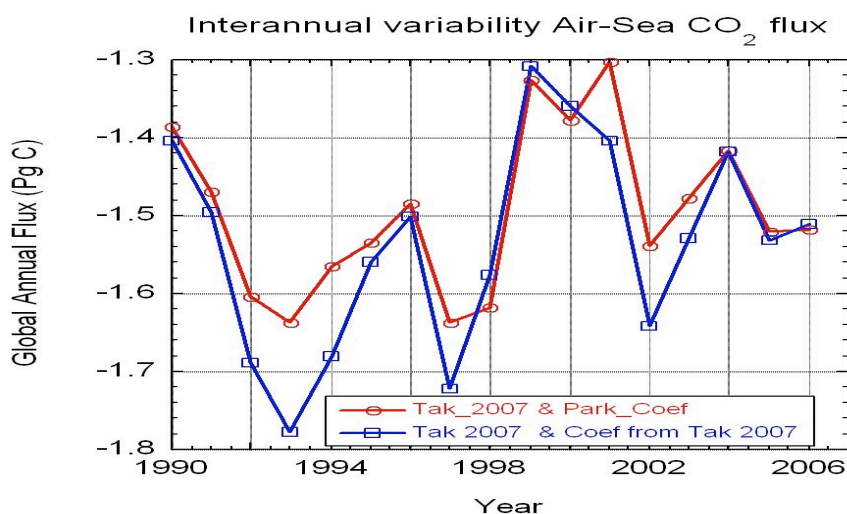


Figure 8: Comparison of estimated interannual variability using monthly sea surface temperature anomalies and the updated global  $\text{pCO}_2$  climatology of Takahashi et al., (submitted). The red line are the results using the SST- $\text{pCO}_2$  relationship derived by Park et al. (2006) while the blue line gives the SST- $\text{pCO}_2$  relationships derived from the new climatology by Trinanes (pers. comm.) as part of this effort.

## Ocean Acidification

Recent laboratory and field studies have provided evidence for deterioration of many species of marine organisms that produce calcium carbonate shells due to increasing carbon dioxide levels in seawater and the resulting decline in pH. For example, increasing seawater acidification has been shown in controlled studies to significantly reduce the ability of reef-building corals to produce their skeletons, affecting growth of individual corals and making the reef more vulnerable to erosion. Some estimates indicate that, by the middle of this century, coral reefs may erode faster than they can be rebuilt potentially making them less resilient to other environmental stresses (e.g., disease, bleaching, storms). The Global Carbon Data Management and Synthesis Project has been providing information directly related to better understanding the effects of ocean acidification and Dr. Richard Feely (PMEL), along with other project PIs, has been actively involved in developing the NOAA strategy for investigating and monitoring ocean acidification and its consequences. We have organized and participated in several national and international conferences on the subject. This is an emerging topic in the ocean community and will likely play a much more prominent role in our interpretation of ocean carbon data in FY08 and beyond.

## REFERENCES

- Broecker, W. and Peng, T.H., 1982. Tracers in the Sea. Eldigio Press, Columbia University, Palisades, NY, 690 pp.
- Broecker, W.S., Peng, T.H., Ostlund, G. and Stuiver, M., 1985. The distribution of bomb radiocarbon in the ocean. *J. Geophys. Res.*, 90(6953-6970).
- Chanson, M. and F.J. Millero, Effect of filtration on the total alkalinity of open-ocean seawater, *Limnol. Oceanogr.: Methods*, 5, 293-295, 2007.
- Johnson, G.C., Robbins, P.E. and Hufford, G.E., 2001. Systematic adjustments of hydrographic sections for internal consistency. *J. Atmos. and Ocean. Tech.*, 18: 1234-1244.
- Key, R.M. et al., 2004. A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP). *Global Biogeochemical Cycles*, 18(4).
- Lee, K.R., Wanninkhof, R., Takahashi, T., Doney, S. and Feely, R.A., 1998. Low interannual variability in recent oceanic uptake of atmospheric carbon dioxide. *Nature* (396): 155-159.
- Levine, N.M., Doney, S.C., Wanninkhof, R., Lindsay, K. and Fung, I.Y., 2007. The impact of ocean carbon system variability on the detection of temporal increases in anthropogenic CO<sub>2</sub>. *J. Geophys. Res.*, in press.
- McNeil, B.I., N. Metzl, R.M. Key, R.J. Matear and A. Corbiere(2007) An empirical estimate of the Southern Ocean air-sea CO<sub>2</sub> flux, *Global Biogeochem. Cycles*, 21(3), GB3011, doi:10.1029/2007GB002991.
- Park, G.-H., Lee, K., Wanninkhof, R. and Feely, R.A., 2006. Empirical ocean temperature-based estimates of variability of oceanic uptake of CO<sub>2</sub> over the last two decades. *Journal of Geophysical Research*, C07S07(111): doi:10.1029/2005JC003090.
- Prentice, I.C. et al., 2001. The carbon cycle and atmospheric CO<sub>2</sub>. In: J.T. Houghton and D. Yihui (Editors), *Climate Change: The Scientific Basis, Contribution of working group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, UK, pp. 183-287.
- Sabine, C.L., R.A. Feely, F.J. Millero, A.G. Dickson, C. Langdon, S. Mecking, J. Swift, and D. Greeley, 2007. Decadal changes in Pacific carbon. *J. Geophys. Res.*, submitted.



- Sweeney, C., E. Gloor, A. R. Jacobson, R. M. Key, G. McKinley, J. L. Sarmiento, and R. Wanninkhof, 2007. Constraining global air-sea gas exchange for CO<sub>2</sub> with recent bomb C-14 measurements, *Global Biogeochemical Cycles*, 21, doi:10.1029/2006GB002784.
- Takahashi, T. et al., 2002. Global sea-air CO<sub>2</sub> flux based on climatological surface ocean pCO<sub>2</sub>, and seasonal biological and temperature effects. *Deep-Sea Research Part II-Topical Studies In Oceanography*, 49(9-10): 1601-1622.
- Takahashi, T., et al., 2007. Climatological Mean and Decadal Change in Surface Ocean pCO<sub>2</sub>, and Net Sea-air CO<sub>2</sub> Flux over the Global Oceans, *Deep -Sea Res.*, submitted.
- Wallace, D.W.R., 2001. Storage and transport of excess CO<sub>2</sub> in the oceans: The JGOFS/WOCE Global CO<sub>2</sub> Survey. In: G. Siedler, J. Church and J. Gould (Editors), *Ocean Circulation and Climate: Observing and Modeling the Global Ocean*. Academic Press, San Diego, CA, pp. 489-521.
- Wanninkhof, R., 1992. Relationship between wind-speed and gas-exchange over the ocean. *J. Geophys. Res.*, 97: 7373-7382.
- Wanninkhof, R. et al., 2007. Decadal changes of carbon and related parameters along meridional section A16 in the Atlantic Ocean. In preparation.

### **FY07 PUBLICATIONS AND REPORTS FROM THIS PROJECT**

- Berelson, W.M., W.M. Balch, R. Najjar, R.A. Feely, C. Sabine, and K. Lee (2007) Relating estimates of CaCO<sub>3</sub> production, export, and dissolution in the water column to measurements of CaCO<sub>3</sub> rain into sediment traps and dissolution on the sea floor: A revised global carbonate budget. *Global Biogeochem. Cy.*, 21, GB1024, doi: 10.1029/2006GB002803.
- Birdsey, R.A., R. Cook, S. Denning, P. Griffith, B.E. Law, J. Masek, A.M. Michalak, S. Ogle, D. Ojima, Y. Pan, C.L. Sabine, E. Sheffner, and E.T. Sundquist (2007) Investigators share improved understanding of the North American Carbon Cycle. *Eos Trans. AGU*, 88(24), doi: 10.1029/2007EO240004.
- Caldeira, K., D. Archer, J.P. Barry, R.G.J. Bellerby, P.G. Brewer, L. Cao, A.G. Dickson, S.C. Doney, H. Elderfield, V.J. Fabry, R.A. Feely, J.-P. Gattuso, P.M. Haugan, O. Hoegh-Guldberg, A.K. Jain, J.A. Kleypas, C. Langdon, J.C. Orr, A. Ridgwell, C.L. Sabine, B.A. Seibel, Y. Shirayama, C. Turley, A.J. Watson, and R.E. Zeebe (2007) Comment on "Modern-age buildup of CO<sub>2</sub> and its effects on seawater acidity and salinity" by Hugo A. Loáiciga. *Geophys. Res. Lett.*, 34, L18608, doi: 10.1029/2006GL027288.
- Chanson, M. and F.J. Millero (2007) Effect of filtration on the total alkalinity of open-ocean seawater, *Limnol. Oceanogr.: Methods*, 5, 293-295.
- Doney, S.C., N. Mahowald, I. Lima, R.A. Feely, F.T. Mackenzie, J.-F. Lamarque, and P.J. Rasch (2007) Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system. *Proc. Nat. Acad. Sci.*, 104(37), 14,580–14,585.
- Dugdale, R.C., F.P. Wilkerson, F. Chai, and R.A. Feely (2007) Size-fractionated nitrogen uptake measurements in the equatorial Pacific and confirmation of the low Si–high-nitrate low-chlorophyll condition. *Global Biogeochem. Cy.*, 21, GB2005, doi: 10.1029/2006GB002722.
- Inoue, H.Y., R.A. Feely, M. Ishii, T. Kawano, A. Murata, and R. Wanninkhof (2006) Long-term trend of the partial pressure of CO<sub>2</sub> in surface waters and sea-air CO<sub>2</sub> flux in the equatorial Pacific. Chapter 1 in *Global Climate Change and Response of Carbon Cycle in the Equatorial Pacific and Indian Oceans and Adjacent Landmasses*, H. Kawahata and Y. Awaya (eds.), Elsevier Oceanography Series, Vol. 73, Elsevier, Amsterdam.

- Lee, K., L.T. Tong, F.J. Millero, C.L. Sabine, A.G. Dickson, C. Goyet, G.-H. Park, R. Wanninkhof, R.A. Feely, and R.M. Key (2006) Global relationships of total alkalinity with salinity and temperature in surface waters of the world's oceans. *Geophys. Res. Lett.*, 33, L19605, doi: 10.1029/2006GL027207.
- Levine, N., M. S. C. Doney, R. Wanninkhof, K. Lindsay, and I. Y. Fung (2007) The impact of ocean carbon system variability on the detection of temporal increases in anthropogenic CO<sub>2</sub>, *J. Geophys. Res.*, in press.
- McGillis (chair and ed.), W., R. Duce, D. Erickson, C. Fairall, D. Farmer, R. Feely, B. Huebert, W. Jenkins, W. Keene, R. Kiene, P. Matrai, K. Melville, W. Miller, R. Najjar, E. Saltzman, P. Schlosser, D. Siegel, W.-J. Cai, D. Ho, S. Doney, K. Johnson, C. McNeil, M.J. Perry, J. Prospero, O. Schofield, P. Shepson, D. Turk, and R. Wanninkhof (2006) The United States Surface Ocean—Lower Atmospheric Study (SOLAS), Science Implementation Strategy. Published in collaboration with the U.S. Ocean Carbon and Biogeochemistry (OCB) program and the International integrated Marine Biogeochemistry Ecosystem Research (IMBER) and SOLAS programs, 123 pp.
- McNeil, B.I., N. Metzl, R.M. Key, R.J. Matear and A. Corbiere (2007) An empirical estimate of the Southern Ocean air-sea CO<sub>2</sub> flux, *Global Biogeochem. Cycles*, 21(3), GB3011, doi:10.1029/2007GB002991.
- Metzl, N., B. Tilbrook, D. Bakker, C. Le Quéré, S. Doney, R. Feely, M. Hood, and R. Dargaville (2007) Global changes in ocean carbon: Variability and vulnerability. *Surface Ocean CO<sub>2</sub> Variability and Vulnerability Workshop, Paris, France, 11–14 April 2007*. *Eos Trans. AGU*, 88(28), 287.
- Millero, F.J., T. B. Graham, F. Huang, H. Bustos-Serrano, D. Pierrot (2006) Dissociation constants of carbonic acid in seawater as a function of salinity and temperature, *Mar. Chem.* 100, 80-94.
- Millero, F.J., The marine inorganic carbon cycle (2007) *Chem. Rev.*, 107, 308-341.
- Millero, F.J., F. Huang, T. Graham, D. Pierrot (2007) The dissociation of carbonic acid in NaCl solutions as a function of concentration and temperature, *Geochim. Cosmochim. Acta*, 71, 46-55, doi:10.1016/j.gca.2006.08.04.
- Reay, D.S., C.L. Sabine, P. Smith, and G. Hymus (2007) Spring-time for sinks. *Nature*, 446(7137), doi: 10.1038/446727a, 727–728.
- Reay, D.S., P. Smith, G. Hymus, and C. Sabine (2007) New Directions: The changing role of the terrestrial carbon sink in determining atmospheric CO<sub>2</sub> concentrations. *Atmos. Environ.*, 41(27), 5813–5815.
- Sabine, C.L., and R.A. Feely (2007) The oceanic sink for carbon dioxide. In *Greenhouse Gas Sinks*, D. Reay, N. Hewitt, J. Grace, and K. Smith (eds.), CABI Publishing, Oxfordshire, UK.
- Sabine, C.L., R.A. Feely, and R. Wanninkhof (2007) 3. Global Oceans; f. Global ocean carbon cycle — in *State of the Climate in 2006*, A. Arguez (ed.). *Bull. Am. Meteorol. Soc.*, 88 (suppl.)(6), S40–S43.
- Sabine, C.L., R.A. Feely, F.J. Millero, A.G. Dickson, C. Langdon, S. Mecking, J. Swift, and D. Greeley (2007) Decadal changes in Pacific carbon. *J. Geophys. Res.*, submitted.
- Sonnerup, R.E., A.P. McNichol, P.D. Quay, R.H. Gammon, J.L. Bullister, C.L. Sabine, and R.D. Slater (2007) Anthropogenic delta<sup>13</sup>C changes in the North Pacific Ocean reconstructed using a multiparameter mixing approach (MIX). *Tellus*, 59B, 303–317.
- Sweeney, C., E. Gloor, A.J. Jacobson, R.M. Key, G. McKinley, J.L. Sarmiento, R. Wanninkhof (2007) Constraining global air-sea gas exchange for CO<sub>2</sub> with recent bomb <sup>14</sup>C measurements, *Global Biogeochem. Cycles*, 21, GB2015, doi:10.1029/2006GB002784, 2007.

- Takahashi, T., S.C. Sutherland, and A. Kozyr (2007) Global Ocean Surface Water Partial Pressure of CO<sub>2</sub> Database: Measurements Performed During 1968 - 2006 (Version 1.0). ORNL/CDIAC-152, NDP-088. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, 20 pp.
- Takahashi, T., S. C. Sutherland, R. Wanninkhof, C. Sweeney, R. A. Feely, D. W. Chipman, B. Hales, G. Friederich, F. Chavez, A. Watson, D. C. E. Bakker, U. Schuster, N. Metzl, H. Yoshikawa-Inoue, M. Ishii, T. Midorikawa, C. Sabine, M. Hopemma, J. Olafsson, T. S. Arnarson, B. Tilbrook, T. Johannessen, A. Olsen, R. Bellerby, H. J. W. d. Baar, Y. Nojiri, C. S. Wong, and B. Delille (2007), Climatological Mean and Decadal Change in Surface Ocean pCO<sub>2</sub>, and Net Sea-air CO<sub>2</sub> Flux over the Global Oceans, Deep -Sea Res., submitted.